Rotationally selected product pair correlation in F + CD 4 DF ( ) + CD 3 (=0, N )
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Rotationally selected product pair correlation in F+CD₄→DF(ν′)+CD₃(ν=0,N)

Jingang Zhou, Weicheng Shiu, Jim J. Lin,⁠¹ and Kopin Liu⁠²

The Institute of Atomic and Molecular Sciences (IAMS), Academia Sinica, P.O. Box 23-166, Taipei, Taiwan 106

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The title reaction was studied in a crossed-beam experiment by imaging of state-selected products. The rotational state selection of the CD₃ products was achieved using (2+1) resonance-enhanced multiphoton ionization (REMPI) technique to ionize the methyl radical products.⁠³ The frequency of the laser was either fixed at the peak⁠¹–⁴ or scanned back and forth over the Q head⁠⁵ while acquiring ion images. In the course of these investigations, we observed some subtle differences in results, depending on whether the laser frequency was scanned or not. Tentatively, we ascribed it to the dependence on the rotational states of the methyl radicals being sampled.⁠⁵ The ascription is, however, somewhat uncertain in view of the comparably small rotation constant [B=4.8 cm⁻¹ for CD₃ (Ref. 7)] and relatively low rotation population of CD₃ products.⁠⁵

Reported in this paper is direct verification of such rotational effects, which in turn demonstrates the active role of the CD₃ rotor in this reaction.

Figure 1 presents the (2+1) REMPI spectrum around the 0₁⁰ band of the CD₃ product from the F+CD₄ reaction at Eᵥ=5.37 kcal/mol. The very intense, central feature is the Q head, which was used in our previous studies.⁠¹–⁴,⁶ The small spectral features on both sides are the N-resolved peaks of the O, P, R, and S branches, respectively. As is seen, the intensities of those N-resolved peaks are, using linearly polarized light, generally weaker than the Q-head signal by 1–2 orders of magnitude. To uncover the N dependence of the pair-correlated attributes, we tuned the laser frequency to the peak of the N-resolved feature⁶ and acquired the ion image at 20 Hz for 2–3 h, accumulating to about 2–3×10⁵ ion events.

Exemplified in Fig. 2(a) is one of the raw images. The REMPI laser was parked at the S(3) transition—i.e., probing the N=3 state. Distinct ring features are clearly displayed.

Nearly identical images were obtained for the two experimental configurations: the linear polarization of the probe laser lied either parallel or perpendicular to the initial relative velocity vector of the collision system. We therefore concluded no rotational alignment effects (in the collision frame) of the results.

Overlaid on the image is the Newton diagram of the collision system; thus, the coincidently formed DF vibrational states are readily assigned. After the density-to-flux transformation,⁠¹ the desired product velocity–flux contour map can be obtained and is presented in Fig. 2(b) in a three-dimensional representation. Similarly, the contour maps for N=5 and 9, when the transitions of O(5) and O(9) were probed, are depicted in Figs. 2(c) and 2(d), respectively. All three contour maps exhibit three ringlike structures corresponding to the coincidently formed DF in ν′=4, 3, and 2, respectively. Yet the appearances of those correlated attributes are significantly different.

The product velocity–flux contour maps shown in Figs. 2(b)–2(d) represent the correlated doubly differential cross

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¹ Also at Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 300.
² Also at Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan 106.

FIG. 1. (2+1) REMPI spectra of the vibrational ground state of CD₃ products from the title reaction at Eᵥ=5.37 kcal/mol. A linearly polarized laser was used. The very intense, central peak is the Q head. The much weaker, N-resolved O, P, R, and S branches are indicated.
sections (DCSs) \( \frac{d^2\sigma}{d\mu d(\cos \theta)} \).\(^9\) Integrating over the relative product speed \( \mu \) within the range of a specific ring yields the vibrationally state-resolved angular distribution of the DF products in coincidence with the “tagged” \( \text{CD}_3 \) rovibrational state. The resultant correlated DCSs for the tagged \( \text{CD}_3 \) states, \( N=3, 5, \) and \( 9 \), are depicted in Fig. 3. The dependences on \( N \) are indeed striking, indicative of the active role of the \( \text{CD}_3 \) rotor in this reaction. For all three \( N \) states, the correlated DF \( (\nu'=4) \) states feature a sharp forward angular distribution superimposed on an isotropic component. In addition, a rainbowlike feature in the small scattering angles prevails with the decrease in \( N \) quantum numbers. The correlated DF \( (\nu'=3) \) states are predominantly backward/sideways scattered, though the protrusion into the forward hemisphere is seen for \( N=9 \). The coincidently formed DF \( (\nu'=2) \) states are essentially characterized by backward scatterings for all three \( N \) states. Compared to those reported previously (Ref. 2, Fig. 3) in which the probe laser was tuned to the peak of the \( Q \) head—namely, \( \langle N \rangle = 4 \)—it is gratifying to note the excellent consistency between those correlated DCSs and the present ones for \( N=3 \) and \( 5 \).

The right lower panel summarizes the correlated angle-dependent energy disposal. The fractional energy disposed into the coincident DF rotor is always small and nearly independent of both the scattered angles and \( N \) states. As a result, the angular dependences of the two remaining degrees of freedom, \( f_{V(DF)} \) and \( f_{T} \), form a mirror image. The fact that the rotational motions of the two molecular products (DF and \( \text{CD}_3 \)) appear largely uncorrelated is somewhat unexpected (vide infra). Intuitively, one might have anticipated some sort of correlation if the two products recoil from impulsive interactions at the transition state.\(^10\) About 75\% of available energy is channeled into the vibration of the DF coproduct. Its angular dependency—more DF vibrational excitation in the forward direction than the backward—is reminiscent of the previous finding for the mode-correlated product pairs in the \( \text{F}+\text{CHD}_2 \) reaction when the product CHD\(_2\) states \( 4_2 \) or \( 3_1 \) were probed.\(^4\) Again, this could be suggestive of the correlation between the impact parameter and scattered angle for a direct reaction with an early barrier, as detailed in the previous report.\(^4\) The variation between different \( N \) states—the solid line for \( N=3 \) and the dotted one for \( N=9 \)—can be traced to the rainbowlike feature in the correlated DCS.

Integrating the state-specific correlated DCS yields the correlated DF vibration branching ratio, and Fig. 4(a) summarizes the results. For ready comparisons between different \( N \) states, we normalized the branching ratios for each \( N \) such that their sum is equal to 1. The correlated vibration branching ratios show a quite remarkable dependence on the tagged \( N \) states: the peaking of the distribution changes from \( \nu'=4 \) for \( N=3 \) to \( \nu'=3 \) for \( N=9 \). The vibrational spacing\(^11\) between \( \nu'=4 \) and 3 is 7.53 kcal/mol and the rotational energy difference between \( N=3 \) and 9 is merely 1.07 kcal/mol.\(^7\) Yet the product pair of the DF \textit{vibrator} (not the DF rotor) and the \( \text{CD}_3 \) \textit{rotor} appears highly correlated. Viewing this correlation in a different way provides further in-
sights. The averaged vibration energy of the DF subensembles \((V_{DF})\), which correlates with a specific \(CD_3\) rotation state, can be calculated from the correlated branching. As is shown in Fig. 4(b), a linear anticorrelation between \((V_{DF})\) and the \(CD_3\) rotational energy \(E_N\) is found with a slope of \(-3.2\). This is to be compared with the anticorrelation between the two vibrators of this reaction, \(DF(v')\) and \(CD_3(r_2)\), in which a slope of about \(-1.0\) was reported. Appropriately, the \(F+CD_4\) reaction proceeds in a way such that the rotation of \(CD_3\) is about 3 times more effective than the \(CD_3\) vibration in compensating the energy disposal into the vibration of the DF coproducts.

It is instructive to examine the implication of this linear anticorrelation between \((V_{DF})\) and \(E_N\). In this experiment, the \(CD_4\) beam is cold from supersonic expansion, so its internal energy is negligibly small. By conservation of energy, one has \(E_c - \Delta H_{\text{st}} = E_{V(\text{CD}_3)} + E_N + E_{v'} + E_{j'} + E_T\). All symbols in this equation have their usual meanings, and the prime (nonprime) indexes refer to the motions of the \(DF(\text{CD}_3)\) products. The vibrational ground state of \(CD_3\) was probed; thus, \(E_{v'} + E_N + E_T = -\Delta H_{\text{st}} + E_c - E_{j'}\). In a very illuminating paper, Schechter et al.\(^{12}\) elucidated kinematic constraints in \(A + BC\) reactive collisions. They argued convincingly that the usual conversion of reactant orbital angular momentum \(l\) to product rotational angular momentum \(j'\) for a heavy + heavy + light system\(^{5}\) should also hold for other mass combination in collinearly dominated reactions due to the steric requirements of the reaction. Hence, one has \(j' \approx al\) under more general conditions, where \(a\) is a dimensionless factor accounting for kinematic constraints.\(^{12}\) For the present polyatomic reaction of \(F+CD_4\), the transition state is believed to be nearly collinear in \(F\cdot\cdot\cdot\cdotD\cdot\cdot\cdotC\) geometry.\(^{13}\)

We assume analogously \(j' \approx al\) for the newly formed DF rotor. Recalling that \(E_j' = Bj'^2\) and \(l^2 = 2\mu b^2 E_c\), thus \(<E_j'> \equiv E_c\), i.e., \(<E_{j'}>(or \langle b^2\rangle)\) is nearly independent of the \(N\) states (vide supra), which is as we found experimentally (Fig. 3). Moreover, the expression for conservation of energy becomes \(E_{v'} + E_N + E_T = \text{const} \sim E_c\), invariant to the selected \(N\) states. The linear relationship between \((V_{DF})\) and \(E_N\) can then be alternatively expressed as \(<E_T'> \equiv C + 2.2E_N\), where \(C\) represents a positive constant.

The conservation of angular momentum can be written as \(l = l' + j' + N\). The assumption \(j' \sim al\) yields \((1 - a)l \sim l' + N\). Squaring it and expressing the terms in the respective energy, one has \(<E_T'> \approx C(E_c - C_2E_N - C_1l \cdot N)\), where the weak \(N\)-dependent parameters have been grouped into three positive constants \(C_1\), \(C_2\), and \(C_3\). Comparing it with the above implied relationship of \(<E_T'> \equiv C + 2.2E_N\), one is led to that \((l' \cdot N)\) is most likely \(N\) dependent and negative. In other words, \(N\) tends to lie antiparallel to \(l'\). As argued previously,\(^{7}\) the present reaction is mainly governed by a coplanar dynamics (in the \(F\cdot\cdot\cdot\cdot\cdotD\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
tionally excited $\text{CD}_3$, etc., are not totally clear. Works addressing those questions are in progress. As elucidated here and in the previous reports, the pair-correlation information offers a powerful vehicle to unravel the “extra-atom” complexity in a typical polyatomic reaction. We hope these works will stimulate further theoretical investigations along this line.

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8 The $K$ structure was not spectrally resolved due to the fast predissociation of the resonant intermediate states in the REMPI process. A previous study (Ref. 5) indicated that the $\text{CD}_3$ products are formed predominantly in the low-$K$ states.